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SYNTHETIC STUDIES IN THE PLEIADENE SERIES

DISSERTATION
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the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By
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** ** ** **

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PART I. METHYLATED PLEIADENES

INTRODUCTION

In recent times, a number of experimental as well as theoretical studies on aromaticity have been made in the field of nonbenzenoid aromatic systems. The reactivity and stability of non-benzenoid \( \pi \)-molecules vary widely. One representative of a non-benzenoid aromatic system is that of pleiadene (1). This compound is interesting because it may be viewed as a benzo-analog of peri-cycloheptanaphthalene (2)\(^2\) which has been found to be stable, or it can be viewed as a perinaphtho-analog of \( \sigma \)-quinodimethane (3)\(^3\) which has been shown to be highly unstable and which exists as a transient species capable of undergoing intramolecular cyclization, Diels-Alder reactions, and dimerization, depending on the conditions under which it is generated.

\[ \text{Diagram of compounds 1, 2, and 3.} \]


\(^3\)M. P. Cava and A. A. Deana, ibid., 81, 4266 (1959).
Pleiadene (1) was first discussed as a hypothetical hydrocarbon and was named by Fieser and Fieser\(^4\) in 1933. In the same year Fieser\(^5\) attempted to generate the methylated pleiadene \(\text{4}\) by heating the corresponding dihydro compound \(\text{5}\) with sulfur, and obtained, instead of the hydrocarbon \(\text{4}\), a sulfide which he proposed has structure \(\text{6}\).

\[
\begin{array}{c}
\text{CH}_3 & \text{CH}_3 & \text{S} & \text{CH}_3 & \text{CH}_3 \\
\text{5} & \text{6} & \text{4}
\end{array}
\]

\(S / \Delta\)

No further attempted syntheses of a pleiadene were then made for nearly two decades. In 1952 Pullman and co-workers,\(^6\) using the molecular orbital method, predicted that the stability of pleiadene (1) would be essentially the same as that of peri-cycloheptanaphthalene (2). Quite recently studies were aimed at the synthesis of pleiadene and its derivatives by D. F. Barringer,\(^7\) who attempted to realize whether such compounds could be isolated as stable species, or whether they possess \(\sigma\)-quinodimethane character. Barringer attempted to generate \(1\)-methylpleiadene (7) by the \(1,4\)-elimination of hydrogen bromide or

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\(^4\)Louis F. Fieser and Mary Fieser, *ibid.*, 55, 3010 (1933). The name pleiadene has recently been adopted as official definitive nomenclature by IUPAC *ibid.*, 82, 5553 (1960).

\(^5\)Louis F. Fieser, *ibid.*, 55, 4977 (1933).


\(^7\)D. F. Barringer, Ph. D. dissertation, The Ohio State University 1959.
water from monobromide 8 or alcohol 9, respectively, and obtained in low yield a hydrocarbon, the structure of which was not elucidated.

While the work discussed in this dissertation was in progress, R. H. Schlessinger was investigating independently the synthesis of the unsubstituted pleiadene (1) both by 1,4-elimination of bromine and sulfur dioxide from dibromide 10 and sulfone 11.

The work reported in this portion of the thesis is concerned with the synthesis of methylated pleiadenes, and it is divided into three parts. A. In order to examine the formation of a pleiadene skeleton by 1,4-elimination of HX (where X = appropriate leaving group) from a mono-substituted substrate, Barringer's attempt to generate 1-methylpleiadene (7) by such an elimination was reinvestigated, and it was hoped to elucidate the structure of his unidentified hydrocarbon. B. The subject of 1,4-elimination of HX described above was

to be extended to a study of the reactions of 1-methyl-7,12-dihydro-
pleiadene-7-one (12) with Grignard reagents, especially in view of
Fieser's early report that an unidentified hydrocarbon was obtained
from the reaction of the monoketone 12 with phenylmagnesium bromide.
Since Fieser's carbon and hydrogen analyses agree reasonably well with
the values calculated for compound 14, it seemed possible that this
hydrocarbon could have been formed by 1,4-elimination of HOH from an
intermediate tertiary alcohol 13; therefore, the Grignard reactions of
monoketone 12 were investigated. It was intended to reinvestigate
Fieser's reaction of dimethyldihydropleiadene 5 with sulfur. If the
sulfide obtained by Fieser has structure 6, it could be converted to
sulfone 15 from which 1,6-dimethylpleiadene (14) might be generated by
extrusion of sulfur dioxide. Thus, a simple synthesis of this hydro-
carbon as well as a structure proof of Fieser's sulfide were to be
attempted.
DISCUSSION OF RESULTS

A. Synthetic Approach to 1-Methylpleiadene

1-Methyl-7,12-dihydropleiadene-7-ol (9) and 1-methyl-7-bromo-7,12-dihydropleiadene (8), from which 1-methylpleiadene (7) would be generated by 1,4-elimination of water or hydrogen bromide, were prepared for the first time by Barringer. The scheme of his synthesis is outlined below. 1-Methyl-7,12-dihydropleiadene-7-one (12) was originally synthesized by Fieser. To obtain this monoketone 12,

Barringer applied Fieser's procedure as shown above, except that in the cyclization step he used liquid hydrogen fluoride as a condensing agent. Fieser had converted the acid 17 into the corresponding acid

chloride and carried out the cyclization with aluminum chloride. Barringer pointed out that this method was quite cumbersome and gave rather poor yields, but the condensation proceeded effectively in anhydrous hydrogen fluoride to give monoketone $12$ in 61% yield.

In the present study it was found that the above Friedel-Crafts reaction of 2-methylnaphthalene with phthalic anhydride gives a mixture of at least two acids as indicated by microcel C. chromatography. This result seems to be in accord with the report by the above two authors that the ketoacid $16$ was difficult to purify and does not form good crystals. To obtain the desired ketoacid unambiguously, the following convenient method of preparation was developed as part of the study described here.

\[ \text{CH}_3 \text{MgBr} \quad + \quad \begin{array}{c} \text{CH}_3 \text{Br} \\ \text{CH}_3 \text{MgBr} \end{array} \quad + \quad \begin{array}{c} \text{CO}_2 \text{H} \\ \text{CO} \end{array} \quad \rightarrow \quad \begin{array}{c} \text{CH}_3 \text{MgBr} \\ \text{CH}_3 \text{MgBr} \end{array} \]

The ketoacid thus prepared was reduced to acid $16$ according to Fieser's method. The cyclization of this acid with hydrogen fluoride, as described by Barringer, gave monoketone $12$ in 75% yield: ketone $12$ was reduced with sodium borohydride to obtain in 100% yield alcohol $2$, which in turn was converted to monobromide $8$ in 81% yield by gaseous hydrogen bromide in benzene, as described by Barringer.
In an attempt to prepare 1-methylpleiadene (7) by the 1,4-elimination of water from alcohol 9, Barringer refluxed a solution of alcohol 9 with excess p-toluenesulfonic chloride in pyridine for two days. The reaction mixture was acidified with hydrochloric acid, and the product was extracted with benzene and crystallized from benzene. There was obtained, in 17% yield, an unidentified hydrocarbon, m.p. 226-227°. Barringer also tried a similar type of elimination by refluxing a solution of monobromide 8 in pyridine for three days and obtained the same hydrocarbon in 11% yield.

Barringer's carbon and hydrogen analyses for this compound (C, 93.59; H, 6.36) gave values intermediate between those (C, 94.18; H, 5.82) calculated for 1-methylpleiadene (7) or a dimer of 7 and those (C, 93.40; H, 6.60) calculated for 1-methyl-7,12-dihydropleiadene (18). His molecular weight determination for the unknown compound by the Rast method gave an average value of 229. Barringer considered the following structures to be possible, but none could be chosen by him definitely because each of these structures was in conflict with part of his data.
Although he admitted that his observed molecular weight (229) was fairly close to that (242) calculated for 1-methylpleiadene (7), he excluded structure 7, since the ultraviolet spectrum of his unknown hydrocarbon was similar to those of alcohol 2, indicating that the unknown compound would not be a fully conjugated hydrocarbon. The dihydro derivative 18 seemed to be also excluded, for the melting point (226-227°) of his hydrocarbon seemed to be too high for a monomer, since similar dihydro compounds 22 and 5 were known to melt at 116.5°\textsuperscript{14} and 133°\textsuperscript{5}, respectively. He pointed out that the closed form 19 was much more likely the structure for his unknown compound,

10A. Reiche, H. Sautoff and O. Muller, Ber., 65, 1371 (1932).
but he observed that the unknown hydrocarbon was recovered unchanged after standing overnight in the presence of N-phenylmaleimide in carbon tetrachloride solution; by contrast, the structurally related 1,2-diphenylbenzocyclobutene reacts with maleic anhydride under these conditions.\textsuperscript{11} He also pointed out that his molecular weight data was not in accord with a dimeric formulation such as the dimer 20 or the coupling product 21.

In the present study, the two reactions described previously were repeated under essentially the same conditions. The crude product from each reaction was chromatographed and crystallized from benzene-ethanol. Both reactions gave the same compound, m.p.245°, as shown by infrared spectra and elemental analysis. The yield was 30\% in the case of the bromide-pyridine reaction and 18\% in the case of the reaction of the alcohol 9 with pyridine and p-toluenesulfonyl chloride. To get additional clues for the structure determination of this unknown hydrocarbon, the isolation of possible intermediates in these reactions was attempted by modifying the reaction conditions. In particular, it was felt that both reactions might proceed via the pyridinium salt 23. In an attempt to prepare this salt, a solution

\begin{align*}
\text{CH}_3 \quad \text{N} & \quad X^- \\
\text{23} & \quad \text{a}, X = \text{Br} \\
& \quad \text{b}, X = \text{Cl}
\end{align*}

\begin{align*}
\text{OTs} \\
\text{24}
\end{align*}

of the bromide B in 2-butanone was cooled in an ice-bath, and an equimolar amount of pyridine was added slowly with stirring. The resulting white crystals, m.p.110-115\(^\circ\), were hygroscopic and failed to give a correct elemental analysis, although they could presumably be the desired pyridinium salt. Since refluxing a pyridine solution of alcohol 2 in the presence of \(p\)-toluenesulfonyl chloride might involve tosylate 2\(\text{H}\) before formation of the pyridinium salt, an attempt was also made to isolate this tosylate by running the same reaction at room temperature. After workup, however, only the starting material 2 was obtained. Because of these results, attempts to use these intermediates to determine the structure of the hydrocarbon were abandoned.

Considering the fact that the unknown hydrocarbon is only moderately soluble in benzene and insoluble in Skelly Solve F, whereas a monomeric hydrocarbon of this type was expected to be readily soluble in these solvents, and because the melting point of the unknown hydrocarbon is quite high, it seemed doubtful that this hydrocarbon could be a monomer. When the molecular weight of the sample was determined osmometrically, it was found to be 62\(\text{H}\), two and a half times as large as the calculated value (2\(\text{H}\)) for monomer 7. This result strongly supports a dimeric structure for the hydrocarbon. It was now necessary to distinguish between two dimeric structures, namely that of the pleiadene dimer 20 and that of the coupling product 21. A choice between these structures could not be made on the basis of nuclear magnetic resonance (n. m. r.) spectroscopy due to the poor solubility
of the compound in the usual solvents. At this time, R. H. Schlessinger prepared a dimer of pleiadene (1) by the elimination of sulfur dioxide from sulfone, and realized that pleiadene (1) was a highly reactive species isolable only as a dimer or as a Diels-Alder adduct.

This data seemed to suggest that the unknown hydrocarbon could be a dimer formed immediately upon generation of 1-methylpleiadene (7) by a 1,4-elimination reaction. Thus, it was decided to synthesize the dimer of 1-methylpleiadene via the route applied by Schlessinger to the synthesis of the parent pleiadene dimer 25. The scheme used is outlined below.
First the monoketone was converted to 1-methyl-7,12-dihydropleiadene-7,12-dione (26) by chromic acid oxidation as reported by Fieser, the structure of this compound was confirmed by its n.m.r. spectrum which showed that the methyl group was intact, while the methylene group was oxidized. The conversion of 1-methyl-7,12-dihydropleiadene-7,12-diol (27) to sulfide 28 by use of phosphorus pentasulfide involved a new method originated by Schlessinger; the mechanism of this transformation is not yet clearly understood. The sulfide thus prepared is a white, crystalline solid, melting at 160-161°.

The n.m.r. spectra of monomethyl sulfide 28 was somewhat unexpected. It shows two unusually separated peaks for the bridgehead protons: one at 4.81τ (singlet, one proton), and the other at 4.38τ (singlet, one proton), whereas the n.m.r. spectrum of the unmethylated sulfide 30 gives only one peak (4.74τ) for the corresponding two protons. Apparently, the C-12 proton in the methyl sulfide is influenced by the nearby methyl group and therefore appears at 4.38τ; in contrast, the C-7 proton appears at the essentially normal position of 4.81τ.

\[ (7.42τ)\text{CH}_3 \quad (4.38τ) \]
\[ \text{CH}_3 \quad \text{H}(4.81τ) \]
\[ \text{H} \quad \text{H}(4.74τ) \]

28

30
A possible explanation for the observed deshielding effect of the methyl group on the C-12 proton may be that the bridged sulfide is quite rigid and the methyl group and C-12 proton are close, as the molecular model shows, and therefore the steric repulsion between the two groups may cause distortion of the electron cloud around the 12-proton nucleus, exposing this nucleus and giving rise to lower field resonance. The steric repulsion between the methyl group and the C-12 hydrogen may be visualized by estimating the distance between the two groups as a measure of the compression involved. From the known van der Waals radii of a methyl group (2.0 Å) and of a hydrogen atom (1.2 Å), and the roughly calculated distance (2.34 Å) between the methyl group and the C-12 hydrogen, the van der Waals compression factor (c-value) was estimated as 0.86. It should be safe to assume that deshielding would occur only when the methyl group and the C-12 hydrogen atom enter into the range of van der Waals interaction (3.2 Å), i.e., the c-value is greater than zero, and therefore, the estimated c-value (0.86) indicates considerable interaction between


13The "compression factor" is the difference in Å between the sum of the van der Waals radii (2.0 Å + 1.2 Å = 3.2 Å) and the measured distance (2.34 Å) between the relevant groups.
the two groups. On the other hand, the c-value for C-6 hydrogen and C-7 hydrogen was shown to be only 0.08, and it is presumed that there is practically no interaction between these two hydrogens. A number of cases of deshielding of a proton by van der Waals interaction in the octahydrophenanthrene series have been reported by Nagata and co-workers,\textsuperscript{14} who have interpreted their results quantitatively in terms of c-values.

The sulfide 28 was converted by peracetic acid oxidation into sulfone 22, a colorless crystalline compound. In an initial experiment to generate 1-methylpleiadene (7) from this sulfone, it was decomposed thermally at 220-240\(^\circ\) in an open test tube. The reaction, which was accompanied by rapid liberation of sulfur dioxide, gave a dimer 20, a white crystalline compound melting at 315-330\(^\circ\), insoluble in Skelly Solve F, and sparingly soluble in benzene. The infrared spectrum of this material was not identical with that of Barringer's unknown hydrocarbon. The ultraviolet spectrum (\(\lambda_{\text{max}} 308\)) of this dimer shows that the absorption maximum has shifted 17 mp to longer

wave lengths, compared to the chromophore in the monomeric dihydrohydrocarbon 18 (λ\text{max} 291) (prepared by LiAlH₄-AlCl₃ reduction ofmoketone 12), indicating a substantial interaction of the II-systems

![Chemical structures](image)

of the two halves of the dimer. The bathochromic shift is similar to that observed (15 mp) for Schlessinger's pleiadene dimer⁸ 25 compared to the corresponding dihydro monomer 22. Such a large bathochromic shift, compared to the same hydrocarbon 18, was not observed for Barringer's unknown hydrocarbon (λ\text{max} 298).

1-Methylpleiadene (7) as an intermediate in the formation ofdimer 20 was confirmed also by a trapping experiment: when the sulfone 29 was decomposed in the presence of N-phenylmaleimide at the same temperature (220–240°C) used to prepare the dimer, a crystalline adduct was obtained. This compound appears to be a single isomer, i.e., it may possess either the exo-configuration 31 or the endo-configuration 32 in view of its sharp melting point (247–248°C). Since Schlessinger has demonstrated⁸ that the corresponding adduct of pleiadene (1) andN-phenylmaleimide has the exo-configuration, the adduct of 1-methylpleiadene described above has been also assigned the exo-
configuration 31.
The irradiation of sulfone 29 in benzene at room temperature gave the same dimer as was obtained by pyrolysis of the sulfone. Finally the result of an elemental analysis agreed with the values calculated for the dimer.

The stereochemistry of 1-methylpleiadene dimer 20 is now mentioned briefly. Because the head-to-head and head-to-tail dimerization are equally probable and because of the methyl group, the following four configurations 33, 34, 35, and 36 of the dimer would be possible. On the basis of a n. m. r. study of his pleiadene dimer 25,
Schlessinger\textsuperscript{8} pointed out that it had the **anti**-configuration \textsuperscript{37} formed by head-to-tail dimerization rather than **syn**-configuration \textsuperscript{38}. By analogy 1-methylpleiadene dimer may have the **anti**-configurations \textsuperscript{33} and \textsuperscript{34}. Since there is no reason to believe that one form, say, \textsuperscript{33} is preferred to the other, it seems probable that the dimer actually obtained, although crystalline, may be an inseparable mixture of two forms \textsuperscript{33} and \textsuperscript{34}.

It has now become clear that Barringer's unknown hydrocarbon cannot be the pleiadene dimer \textsuperscript{20}. It seemed likely, therefore, that this compound was the coupling product \textsuperscript{21}. Thus an independent synthesis of the coupling product was attempted. When a solution of the monobromide \textsuperscript{8} was refluxed with copper powder for 24 hours, small white crystals of a hydrocarbon, m.p.260\textdegree, were obtained in 71\% yield.
The infrared spectrum of this compound was identical with that of Barringer's unknown hydrocarbon obtained from previous reactions. The difference in melting points may be considered to be a matter of purity. Reviewing now the results of Barringer's original analysis for his hydrocarbon, it was evident that he obtained the correct values for a coupling product, but his erroneous molecular weight data unfortunately led him astray in the choice of a structure.

Interestingly, the absorption maximum ($\lambda_{\text{max}} 298$) of the coupling product 21 has shifted 7 mp to longer wavelengths, compared to its monomer 1-methyl-7,12-dihydropleiadene (18) ($\lambda_{\text{max}} 291$), although the shift in the absorption maximum is less prominent, compared to that for the pleiadene dimer 20 ($\lambda_{\text{max}} 308$). This data indicates that there may be a partial interaction of the π-systems of the two halves of the coupling product, and it is highly probable that such an interaction of the π-clouds is attributed to a partial folding of the two halves within the molecule.

Although the mechanisms of the original synthesis of Barringer's hydrocarbon are not completely clear, the following processes seem plausible:
Since these mechanisms had not been conceived when the reactions were carried out, no attempts were made to isolate the postulated by-product dipyridyl (40). If this mechanism is correct, it is quite surprising that the pyridinium salt did not undergo 1,4-elimination to give a pleiadene under such a forced condition as refluxing in pyridine, but rather resulted in the formation of a free radical 39.
B. Reactions of 1-Methyl-7,12-dihydropleiadene-7-one

with Grignard Reagents

As an extension of the work which has been just described, a brief study on the reactions of monoketone 12 with Grignard reagents has been made.

When the monoketone 12 was allowed to react with phenylmagnesium bromide in ether for five hours at room temperature and the reaction mixture was worked up under mild conditions, there were obtained three products 41, 42, and 13, which were separated by chromatography.
The major product, obtained in 45% yield, was assigned the structure \( h_2 \) and the second product was assigned the structure \( l_3 \). The third product, obtained in very small amount, is believed to be the \( \alpha, \beta \)-dihydroketone \( h_1 \) which could have given the ketone \( h_2 \) by air oxidation during workup. In contrast to Fieser's claim\(^1\) that a pale yellow hydrocarbon, m.p. 237\(^0\), was obtained as the sole product of this same reaction (neither the reaction conditions nor the yield was described), no such hydrocarbon was found in the present study.

The 1,4-addition products \( h_1 \) and \( h_2 \) and the tertiary alcohol \( l_3 \) were identified by spectral data. The conjugated ketone \( h_2 \) has an absorption maximum at 340 mp, as compared to an absorption maximum of 350 mp for 1-methyl-7,12-dihydropleiadene-7-one (12), whereas the dihydro compound \( h_1 \) has no maximum in this region, but gives only an indefinite curve between 250-300 mp. It would ordinarily be expected that the observed maximum for the phenylated ketone \( h_2 \) would appear at a longer wavelength than that of the parent ketone 12. Since this is not the case, it must be assumed that the phenyl group in the ketone \( h_2 \) is forced out of the plane of the naphthalene ring by the adjacent carbonyl. The n. m. r. spectrum of the ketone \( h_2 \) shows, besides a low-field multiplet for 14 aromatic protons, a singlet (3 protons for C-1 methyl) at 7.32\( \tau \) and a singlet (2 protons for C-12 methylene). Sodium dichromate oxidation of this ketone gave 1-methyl-7-phenyl-7,12-dihydropleiadene-7,12-dione (43), the structure of which was confirmed by the absence of the peak for two C-12 methylene protons in the n. m. r. spectrum as compared to that of the parent ketone \( h_2 \). The structure of dihydroketone \( h_1 \) could not be proven on the basis
of n. m. r. data due to lack of sufficient material, but the fact that a small sample of this compound, when treated with chloranil, gave aromatized ketone 42 suggests that the original ketone has structure 41. The tertiary alcohol 13 shows a hydroxyl band at 3550 cm\(^{-1}\). Its n. m. r. spectrum is also in agreement with the structure 13.

The fact that 1,4 addition of phenylmagnesium bromide gives the ketone 42 (via 41) is rather unexpected. The molecular model of 1-methyl-7,12-dihydropleiadene-7-one (12) shows that the carbonyl group is hindered from behind by the two aromatic hydrogens at C-6 and C-8, and hindered in front by one of the C-12 methylene hydrogens,

and thus 1,4 addition predominates. The steric effect of the C-12 methylene group was demonstrated by comparing with the Grignard
reaction of 7,12-dihydro-7,12-dione (44)\textsuperscript{15} in which 7,12-dihydro-7,12-diphenyl-7,12-dihydropleiadene-7,12-diol (45) was the only product (yield, 40\%) under similar conditions.

Analogous reactions of sterically hindered ketones with Grignard reagents are known. For example, Fuson and Sauer\textsuperscript{16} have reported that addition of methylmagnesium iodide to 1,3-dimesitoylbenzene (46) resulted in the 1,4 addition product 47.

\begin{align*}
\text{MesCO} & \quad \text{CH}_3\text{MgI} \quad \text{MesCO} \\
\text{COMes} & \quad \text{CH}_3\text{H} \quad \text{COMes} \\
\text{46} & \quad \text{COMgI} \\
\text{MesCO} & \quad \text{H}^+ \\
\text{COMes} & \quad \text{47}
\end{align*}

The reaction of the monoketone 12 with methylmagnesium bromide is also interesting. When the ketone was allowed to react with this Grignard reagent in ether at room temperature for 5 hours in one

\textsuperscript{15}This diketone was furnished by Dr. R. H. Schlessinger.\textsuperscript{8}

case, and 24 hours in another case, the starting material remained unchanged, although an amorphous product was found in small amount. When the reaction was carried out in tetrahydrofuran at reflux for 24 hours there were isolated, besides the unchanged ketone 12, exo-methylene compound 48 in 19% yield and 2,6-dimethyl-7,12-dihydro-

![Chemical structures]

pleiadene 7-one (49) in less than 1% yield. The dimethylketone 49 must have been formed by 1,4 addition of the reagent, followed by air oxidation of \( \omega,\beta \)-dihydro ketone. The exo-methylene compound 48 should be the result of 1,2-elimination of water during workup from the initially formed tertiary alcohol 13.

This new hydrocarbon was identified as follows: the infrared spectrum gave a strong band at 11.15 for a disubstituted olefin. The ultraviolet spectrum showed that the absorption maximum was shifted 15 m\( \mu \) to a longer wavelength compared with that of 1-methyl-7,12-
dihydropleiadene, indicating that conjugation was increased. The n.m.r. spectrum gave, besides a multiplet for the aromatic protons, a singlet (3 protons for C-1 methyl) at 7.39τ, a singlet (2 protons for C-12 methylene) at 5.67τ, a doublet (J = 2 c.p.s., 1 proton) at 4.76τ, and a doublet (J = 2 c.p.s., 1 proton) at 4.33τ. The latter two doublets, which must represent the absorption of the two olefinic protons, are separated by 0.43 ppm. The separation of these protons

\[
\begin{align*}
\text{CH}_3 & \quad \text{H} \quad \text{H} \\
& \quad \text{H} \quad \text{C} \\
4.33\tau & \quad \text{H(a)} \\
4.76\tau & \quad \text{H(b)} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{C} = \text{C} \\
& \quad \text{H(d)} \\
4.95\tau & \\
4.64\tau & \quad \text{H(c)} \\
\end{align*}
\]

may be explained by the different ring current effects of the benzene and naphthalene systems. It has been observed that in \(\alpha\)-methylstyrene \cite{17} the \(\beta\) proton (c) which is cis to phenyl group is more deshielded (4.64τ) than the other proton (d) which is trans to the phenyl group. Such deshielding of the proton (c) is due to the ring current effect of benzene, and similar magnetic anisotropy should be observed in the comparable olefinic proton (b) in compound \(\text{48}\). Because the 4.76τ is close to the \(\tau\)-value (4.64τ) for the proton (c), the peak at 4.76τ

\[\text{See High Resolution n.m.r. Spectra Catalog, Varian Associates (1962), pp. 231, 232.}\]
is assigned to the proton (b) which is on the same side as the benzene ring and the peak at 4.33\(\tau\) to the proton (a) lying on the same side as the naphthalene ring.

It is assumed that naphthalene has greater ring current effect than benzene, giving the lower \(T\)-value for the proton (a). Such a difference in \(T\)-values (4.76 and 4.33), however, seems too great to be ascribed solely to the difference in ring current effects of the two \(\pi\)-systems. It may be that the ring systems are tilted so that the proton (b) does not lie as much at the side of the aromatic ring as does the corresponding proton (a), thus causing a greater difference in deshielding than might be expected.

The coupling of protons (a) and (b) is in accord with their different chemical environments, and the observed coupling constant \((J = 2 \text{ c.p.s.})\) is of the expected magnitude.\(^{18}\)

Since the tertiary position is crowded and a readily removable methyl proton is available in the tertiary alcohol \(^{50}\), the dehydration is facilitated even under such mild conditions as workup with aqueous ammonium chloride. The dehydration, which probably involves carbonium ion \(^{52}\) takes place by 1,2-elimination to form the exo-methylene compound \(^{48}\), rather than by 1,4-elimination which would generate 1,7-dimethylpleiadene \(^{53}\). It is interesting that the methylene derivative \(^{48}\), even if formed initially, does not rearrange readily to the isomeric pleiadene \(^{52}\); the latter compound probably have been detected readily as a dimer.

In the case of the phenyl tertiary alcohol 13, carbonium ion 54, which should be generated readily, could lead to the formation of 1-methyl-7-phenylpleiadene (14) by 1,4-elimination. The fact that this tertiary alcohol survives under conditions leading to the formation of the methylene compound 48 indicates that elimination of a C-12 proton from the possible intermediate 54 does not take place readily.

As mentioned earlier, Fieser's unknown hydrocarbon (m.p. 237; Anal. C, 93.83; H, 5.83) was not found among the reaction products of the monoketone 12 with phenylmagnesium bromide. Without knowing the reaction conditions used by Fieser and the conditions under which the reaction mixture was worked up, it is not easy to say what the structure
of his hydrocarbon might be. Although the elemental analysis agrees with the values (C, 94.30; H, 5.70) calculated for the hydrocarbon $\text{I}_4$, it is unlikely that his hydrocarbon could be a pleiadene $\text{I}_4$ or a pleiadene dimer in view of the presently observed reluctance to 1,4-elimination of HOH or HBr in various dihydropleiadene derivatives. Furthermore, if the pleiadene $\text{I}_4$ was generated, it would be most likely isolated as a dimer, and its melting point of which should be much higher than 237°, since the dimers of 1-methylpleiadene (7) and pleiadene (1) have been found to melt at 315°-330° and 350°-370°, respectively.

If Fieser worked up his reaction mixture under strongly acidic conditions, it might be possible that his unidentified hydrocarbon formed from the tertiary alcohol $\text{I}_3$ by elimination of water. Thus, the alcohol $\text{I}_3$ was heated with formic acid on the steam bath for 20 minutes. The resulting crystalline compound, m.p. 240° gave an

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19 On addition of formic acid to the tertiary alcohol, a purple-red solution resulted. The solution turned blue while heating, then yellow. Crystals were collected from the permanently yellow solution.
infrared spectrum characteristic of hydrocarbon. The n.m.r. spectrum (Fig. III-15) of this material showed, besides a multiplet for the aromatic protons, a singlet at 7.31 τ (3 C-1 methyl protons), a doublet (J = 3 c.p.s.) at 5.41 τ (2 C-12 protons), and a singlet at 4.05 τ (1 C-7 proton). This spectrum is in accord with structure 55. The result of elemental analysis (C, 94.00; H, 5.61) agrees both with the values (C, 93.30; H, 5.70) calculated for the structure 55 and with Fieser's analytical data (C, 93.83; H, 5.83) for his unidentified hydrocarbon. Furthermore, the melting point (240°) of this compound is close to that (237°) reported by Fieser. From these observations, it is highly probable that Fieser's unidentified hydrocarbon was the cyclized product 55, which can be thought of as forming in the following manner:

\[ \text{54} \xrightarrow{\text{CH}_3} \text{56} \xrightarrow{\text{57}} \text{55} \]
C. Generation of 1,6-Dimethylpleiadene

The synthesis of dimethylpleiadene \( \text{4} \) was investigated in connection with a proof of the structure of Fieser's sulfide \( \text{6} \) (see p. 2). If the latter compound had the structure \( \text{6} \) originally assigned to it, it could serve as an intermediate in a simple three-step conversion of a dihydropleiadene \( \text{5} \) to the corresponding pleiadene \( \text{4} \).

The hydrocarbon precursor \( \text{5} \) of Fieser's sulfide was originally prepared by Fieser\(^\text{4, 9}\) by the scheme shown below:

![Chemical diagram]
In the present study this method was applied to the synthesis of the hydrocarbon \( \mathcal{E} \) with the following modifications:

During the chromatography of the crude material obtained in the HF – cyclization step, there were found, besides the major product dimethylmonoketone \( \text{49} \), a small amount of at least two ketones, which were characterized only by their infrared spectra. This observation indicates that in the phthaloylation step ketoacid \( \text{52} \) was contaminated by a small amount of at least two isomeric ketoacids.

The dimethylketone \( \text{49} \) was identical in every aspect with the ketone formed by 1,4-addition of methylmagnesium bromide to methyl ketone \( \text{12} \) (Section B). This observation offers direct support of the 1,4-addition mechanism of Grignard reagents to ketone \( \text{12} \).

The reaction of hydrocarbon \( \mathcal{E} \) with sulfur was carried out according to Fieser to obtain a sulfide in about 30% yield with properties similar to those reported by him. Although Fieser suggested that the structure of this sulfide was \( \text{6} \) on the basis of elemental analysis, it seemed also possible that it might have the alternative structure \( \text{62} \). In order to distinguish between these
two structures, the sulfide having the unambiguous structure 6 was synthesized via the route shown below:

Thus, the monoketone 49 was converted to diketone 63 by chromic acid oxidation according to Fieser; the structure of this diketone was confirmed by its n. m. r. spectrum which showed that the two methyl groups were intact, while the methylene group was oxidized. 2,6-Dimethyl-7,12-dihydropleiadene-7,12-diol (64) which was obtained from the sodium borohydride reduction of the diketone 63 was not known previously. Although analytically pure material 64 was not obtained, the sulfide 6 resulting from the reaction of the diol with phosphorus pentasulfide was analytically pure. The sulfide thus prepared was
identical in every respect with that from the hydrocarbon-sulfur reaction, proving that Fieser's proposed structure is correct. The structure of this bridged sulfide was further confirmed by its n. m. r. spectrum, which shows besides a multiplet for the aromatic protons, a singlet (7.39 τ) for two methyl protons, and a singlet (4.38 τ) for two bridgehead protons. As expected, the two bridgehead protons resonate at the same field (4.38 τ), whereas the corresponding two protons in monomethyl sulfide 28 resonate at different fields (4.38 τ and 4.81 τ) as described previously; the τ-value for the two protons in the dimethyl sulfide 6 is exactly the same as that for the proton at the C-12 position monomethyl sulfide 28. This observation gives additional support to the interpretation that the lower field resonance of the C-12 proton in monomethyl sulfide 28 is due to van der Waals repulsion by the methyl group, which causes deshielding of the C-12 proton.

![Chemical Structures](image)

Such a deshielding effect due to steric repulsion was not observed, however, in the parent hydrocarbons of these sulfides, since the two bridgehead protons of both 5 and 18 give only one peak: 5.58 τ (singlet, 2 protons) for monomethyl hydrocarbon 18 and 5.60 τ.
(singlet, 2 protons) for dimethyl hydrocarbon (5). This may be explained by arguing that these hydrocarbon molecules can flip back and forth

\[
\begin{align*}
(7.45\tau) & \quad \text{CH}_3 \quad (5.58\tau) \\
& \quad \text{H} \quad \text{H} \\
(5.58\tau) & \quad \text{H} \\
\end{align*}
\]

at the C-7 and C-12 positions to reduce the steric repulsion.\(^\text{20}\) The essentially same magnitude of the \(\tau\)-values of the C-1 methyl protons in both of the bridged sulfides and in their parent hydrocarbons suggests that the methyl protons in the sulfides are not appreciably deshielded in spite of their interaction with the bridgehead hydrogen. This may be due to the fact that the methyl group is quite bulky, and therefore, the repulsion by a small bridgehead hydrogen would not cause much deshielding of the methyl protons.

2,6-Dimethyl-7,12-dihydropleiadene-7,12-sulfone (15) was prepared by peracid oxidation of the dimethyl sulfide. It was expected that

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2,6-dimethylpleiadene (I) could be generated from the sulfone 15 in the same way that 1-methylpleiadene (7) had been generated from the corresponding sulfone 29 (Section A). Thus, the pleiadene I was thermally generated at 220°-240° to obtain dimer 66. This dimer was identical with that obtained by photolysis of the sulfone 15 at room temperature. An experiment to trap 2,6-dimethylpleiadene (I) as an intermediate was carried out by decomposing the sulfone at 220°-240° in the presence of N-phenylmaleimide to give a Diels-Alder adduct 65. These results are summarized below:
From the considerations used in the assignment of stereochemistry of structures to the N-phenylmaleimide adduct and to the dimer of 1-methypleiadene (7), the N-phenylmaleimide adduct of 2,6-dimethylpleiadene (6) and the 2,6-dimethylpleiadene dimer were assigned structure 65 and 66 respectively.
EXPERIMENTAL

1-Bromo-2-Methylnaphthalene –- This compound was prepared by the procedure of Adams and Binder. To a solution of 2-methylnaphthalene (142 g., 1.0 mole) in carbon tetrachloride (300 ml.) were added a crystal of iodine and a pinch of iron powder. The flask and contents were cooled to 0°. The flask was covered with a towel to exclude light, and bromine (160 g., 1.0 mole) in carbon tetrachloride (300 ml.) was added, with mechanical stirring, over a period of eight hours. The temperature was not allowed to rise above 5°. After standing overnight, the black carbon tetrachloride solution was washed with aqueous sodium bisulfite with water and then dried over anhydrous magnesium sulfate. The resulting pale red solution was distilled under reduced pressure (3-5 mm.). The fraction b.p. 128°-135° was collected and chromatographed over grade I Woelm neutral alumina, giving a yellow oily product (133.65 g., 61%), b.p. 128°-130° at 5 mm., lit. 152°-156° (14 mm.).

2-Methyl-1-naphthylmagnesium bromide –- A mixture of magnesium (12.5 g.) and 1-bromo-2-methyl naphthalene (about 20 g.) was covered

Melting points are uncorrected. Alumina used for chromatography is grade II (3% water) Woelm Alumina, unless otherwise specified. Analyses were carried out by Midwest Microlab, Inc., Indianapolis, Indiana, and Alfred Berhardt Mikroanalytishes Laboratorium, Mulheim, Germany. Photolysis experiments used the full spectrum of a water cooled Hanovia type 79 A 36 mercury arc lamp contained in a quartz probe.

with dry ether and the reaction initiated by addition of a few drops of methylmagnesium bromide followed by gentle warming. After the reaction started, the remainder of the bromide (to total 133.65 g.) in dry ether (150 ml.) was added with stirring. The reaction mixture was allowed to reflux for 30 minutes after the addition was complete. The ether was decanted and the white precipitate which formed was dissolved in dry benzene (200 ml.).

\[ \text{2(2'-Methyl-1'-naphthyl) benzoic acid (16).} \]

- To a well stirred refluxing suspension of phthalic anhydride (11.8 g., 0.1 mole) in dry toluene 2-methyl-1-naphthylmagnesium bromide (24.6 g., 0.1 mole) was introduced via a dropping funnel at a rate of 5 ml. per minute. After addition of the reagent was complete, the reaction mixture was allowed to reflux for 3 hours and then cooled to room temperature. The light yellow salt which precipitated was collected by filtration, dried, and hydrolized by slowly adding it to dilute hydrochloric acid (200 ml.). The granular precipitate collected by filtration of the suspension was washed with water, dissolved in ether and the keto acid extracted with aqueous sodium bicarbonate. The alkaline solution was acidified with dilute hydrochloric acid and the resulting crude acid was dried (yield: 21.4 g., 73.8\%). The keto acid was used without purification in the next step.

\[ \alpha-(2-Methyl-1-naphthyl)-o-toluic acid (17). \]

- The crude 2-(2'-methyl-1'-naphthyl) benzoic acid (50 g.) from the preceding reaction was dissolved in a solution of sodium hydroxide (75 g.) in water (1 l.). To this solution was added zinc dust (150 g.), and the
resulting mixture was heated on the steam bath for three days. After removing the solid from the reaction mixture by filtration, the solution was acidified with dilute hydrochloric acid, resulting in the precipitation of crude product which, after filtration, was digested with hot water. The acid was crystallized from benzene and a small amount of Skelly Solve B to obtain a light tan powder (31.2 g., 65.7%), m.p. 188°-190°; lit. 9 187°.

1-Methyl-7,12-dihydropleiadene-7-one (12) -- To χ-(2-methyl-1-l-naphthyl)-o-toluic acid (17) (20 g.) in polyethylene bottle, anhydrous liquid hydrogen fluoride (about 450 ml.) was added. The dark purple solution was allowed to stand for three days while the hydrogen fluoride evaporated. The residue was treated with 10% aqueous sodium carbonate to neutralize any remaining acid, and from the resulting mixture of solid and alkaline solution, the product ketone was extracted with benzene. The dark brown benzene solution was washed with water, dried over anhydrous magnesium sulfate and concentrated. Preliminary purification was effected by passing the concentrate through a column of charcoal (30 g.) and "Supercel" (60 g.), using benzene as an eluting solvent.

The resulting benzene solution was concentrated and chromatographed on alumina using benzene as the developing agent.

After evaporation of the solvent from the eluent solution, the residue was crystallized from benzene Skelly Solve F, yielding white needles (14 g., 75%), m.p. 133°-134°; lit. 128°.
1-Methyl-7,12-dihydropleiadene-7-ol (9) — To a solution of 1-methyl-7,12-dihydropleiadene-7-one (3.000 g.) in absolute ethanol (100 ml.) was added sodium borohydride (3 g.). The reaction mixture was allowed to heat on a steam bath until dissolution of the reagent was complete, and then to stand overnight at room temperature, after which water (100 ml.) was added. Hydrolysis was completed by gently heating on the steam bath for one hour. The white fabrous crystals which accumulated on cooling were collected by filtration and washed with water. Recrystallization from aqueous ethanol yielded white fabrous needles (3.007 g., 99.5%), m.p. 154°-155°.

1-Methyl-7-bromo-7,12-dihydropleiadene (8) — Gaseous hydrogen bromide was bubbled through a solution of 1-methyl-7,12-dihydropleiadene-7-ol (2.000 g.) in benzene (50 ml.) for 10 minutes. The solution was allowed to stand for two hours and the solvent evaporated. To the condensed benzene solution was added cyclohexane yielding light green crystals (2.017 g., 80.5%), m.p. 163°-164°.

Coupling product of 1-Methyl-7,12-dihydropleiadene (21) — This compound was obtained in three different ways.

Method A: To the solution of 1-methyl-7-bromo-7,12-dihydropleiadene (0.500 g.) in benzene (125 ml.) was added a pinch of copper powder. The resulting mixture was allowed to reflux for 2½ hours, after which it was filtered, concentrated, and chromatographed on alumina using benzene as the eluting solvent. Crystallization from benzene-ethanol yielded white powdery crystals (0.266 g., 70.6%), m.p. 260°.
Anal. Calcd. for C_{38}H_{30}: C, 93.79; H, 6.21

Found: C, 93.61; H, 6.59

Method B: 1-Methyl-7-bromo-7,12-dihydropleiadene (8) (1 g.)
was dissolved in pyridine and refluxed for 40 hours. The solution
was acidified with dilute hydrochloric acid and the hydrocarbon was
extracted with benzene and chromatographed on alumina. Crystalliza-
tion from benzene-ethanol gave material (0.228 g., 30.2%), identical
in every aspect with that prepared via method A.

Method C: 1-Methyl-7,12-dihydropleiadene-7-ol (9) (0.710 g.),
and p-toluenesulfonyl chloride (0.70 g.) were dissolved in pyridine
(25 ml.) and refluxed for 45 hours. After cooling to room tempera-
ture and acidification of the reaction mixture with hydrochloric acid,
the hydrocarbon was extracted with benzene and chromatographed on
alumina. Crystallization was effected from benzene-ethanol, yielding
crystalline solid (0.120 g., 18.0%), identical with that obtained via
methods A and B.

1-Methyl-7,12-dihydropleiadene-7,12-dione (26) — To the solu-
tion of 1-methyl-7-pleiadene (4.000 g.) in glacial acetic acid (250 ml.)
was added sodium dichromate (6.4 g.). After allowing the solution to
reflux for 3 hours and to cool to room temperature, the product was
extracted with methylene chloride from the reaction mixture. The solu-
tion was dried over anhydrous magnesium sulfate, concentrated, and
chromatographed on alumina, using methylene chloride as the eluent.
Crystallization from methylene chloride and a small amount of Skelly
Solve F yielded slightly yellow needles (2.803 g., 66.4%), m.p.
178°-179°; lit.¹ 183°.
1-Methyl-7,12-dihydropleiadene-7,12-diol (27) — To the solution of 1-methyl-7,12-dihydropleiadene-7,12-dione (26) (1.500 g.) in absolute ethanol (100 ml.) was added sodium borohydride (3 g.). The mixture was heated on a steam bath until dissolution of the reagent was complete and allowed to stand at room temperature overnight. Water (100 ml.) was added, and hydrolysis completed by heating on a steam bath for one hour. The white granular product was collected by filtration and washed with water. Crystallization from aqueous acetone yielded white needles (1.254 g., 82.0%), m.p. 213°-215°.

Anal. Calcd. for C_{19}H_{25}O: C, 82.58; H, 5.81
Found: C, 82.72; H, 5.99

1-Methyl-7,12-dihydropleiadene-7,12-sulfide (28) — A heterogeneous mixture of 1-methyl-7,12-dihydropleiadene-7,12-diol (27) (1.000 g.), phosphorus pentasulfide (about 1 g.), and carbon disulfide (50 ml.) was stirred at room temperature for 50 hours. The reaction mixture was then shaken with benzene (50 ml.) and filtered with the aid of vacuum through a celite pad to give clean yellow solution. The solvent was removed and the residue was chromatographed on grade I alumina, using benzene as the eluent. Crystallization from benzene yielded pale white prisms (0.787 g., 74.4%), m.p. 160°-161°.

Anal. Calcd. for C_{19}H_{14}S: C, 83.20; H, 5.15; S, 11.65
Found: C, 82.96; H, 5.06; S, 11.54

1-Methyl-7,12-dihydropleiadene-7,12-sulfone (29) — A solution of 1-methyl-7,12-dihydropleiadene-7,12-sulfide (28) (0.500 g.) in glacial acetic acid (20 ml.) was cooled to room temperature. To the
solution was slowly added peracetic acid (10 ml.) while stirring. The reaction mixture was stirred at room temperature for 3½ hours. Water (25 ml.) was added and the white crystals formed were collected by filtration, washed with water, and dried, giving a crude product (0.489 g., 87.6%). Crystallization from methylene chloride—Skelly Solve F gave colorless prisms, m.p. 220°-240° (dec.).

Anal. Calcd. for C_{19}H_{14}SO_2: C, 74.45; H, 4.61; S, 10.45
Found: C, 74.48; H, 4.69; S, 10.20

Diels-Alder adduct 31. of 1-Methyl-7,12-dihydropleiadene-7,12-sulfone (29) and N-Phenylmaleimide — A mixture of the sulfone (0.1000 g.) and N-phenylmaleimide (0.0563 g., 1 equivalent) in a small open test tube was allowed to heat in a salt bath at 220°-240° for 1 minute. The resulting reaction mixture (yellow solid) was chromatographed on alumina using benzene as a developer. Crystallization from benzene-Skelly Solve F yielded white crystals (0.0815 g., 60.5%), m.p. 247°-248°.

Anal. Calcd. for C_{29}H_{21}N_O_2: C, 83.83; H, 5.09; N, 3.37
Found: C, 84.22; H, 5.04; N, 3.50

Dimer 20. of 1-Methylpleiadene (7): A Thermolysis of Sulfone 29 — 1-Methyl-7,12-dihydropleiadene-7,12-sulfone (29), (0.120 g.) in a small test tube was allowed to heat in a salt bath at 220°-240° for 2 minutes. The crude product was dissolved in a large amount of benzene (sparingly soluble), placed on grade I alumina column, and developed with the same solvent. Crystallization from benzene-ethanol yielded slightly yellow white crystals (0.0045 g., 26.1%), m.p. 315°-330°.
Anal. Calcd. for C_{38}H_{28}: C, 94.18; H, 5.82
Found: C, 93.88; H, 5.98

B. Photolysis of Sulfone (29) — A solution of 1-methyl-7,12-dihydropleiadene-7,12-sulfone (29) (0.100 g.) in benzene (180 ml.) was irradiated with a mercury arc at 20° under nitrogen atmosphere for one hour. The resulting solution was concentrated, chromatographed and crystallized as described in A to give white needles (0.020 g., 12.6%), m.p. 315°-330°. This product was identical in every respect with the compound obtained by pyrolysis of sulfone (29).

1-Methyl-7,12-dihydropleiadene (18) — 1-Methyl-7,12-dihydropleiadene-7-one (12) (3.000 g.) in a Soxhlet cup, (200 ml.) was extracted into a suspension of lithium aluminum hydride (2 g., excess) and aluminum chloride (2 g.) dissolved in dry ether (50 ml.). The reaction mixture was allowed to reflux under the Soxhlet extractor for 48 hours. Water (100 ml.) was introduced slowly into the reaction flask to hydrolyze the reaction mixture. The two-phase system was poured into concentrated hydrochloric acid (100 ml.). The organic layer was diluted with benzene (100 ml.), partitioned, washed with water, and dried over anhydrous magnesium sulfate. The yellow oily residue obtained on evaporation of the solvent was chromatographed on alumina with benzene as eluent. The eluent solution from the blue fluorescent band (UV lamp) was condensed and crystallization was effected by addition of absolute ethanol, yielding thin white plates (2.23 g., 78.5%), m.p. 78°-79°.

Anal. Calcd. for C_{19}H_{16}: C, 93.40; H, 6.60
Found: C, 93.16; H, 6.59
Reaction of l-methyl-7,12-dihydropleiadene-7-one (12) with phenyl-
magnesium bromide — To a solution of l-methyl-7,12-pleiadene-7-one
(12) (0.500 g.) in dry ether (50 ml.) was added 3 M. phenylmagnesium
bromide (3 ml.), and the mixture was stirred for 5 hours at room
temperature. The resulting reaction mixture was hydrolyzed with
aqueous ammonium chloride (50 ml.). After adding benzene (100 ml.)
to the hydrolysis mixture, the organic layer was separated, washed
with water, and dried over anhydrous magnesium sulfate. The residue
obtained on evaporation was chromatographed on alumina using benzene
as a developer. The column gave a blue band followed by a pale,
light green-blue band.

(a) \(\alpha,\beta\)-Dihydroketone \(\text{Ll}\) — The eluent solution from
the blue band (1st band) gave white crystals (about 15 mg., 2\%)
crystallization from benzene-Skelly Solve F) m.p. 110\(^\circ\)-111\(^\circ\); \(\nu\text{co} = 1670\text{cm}^{-1}\). The UV spectrum did not appear to be characteristic,
giving a curve of no maxima between 250-300 \(\mu\). N.m.r. and analyti-
cal samples were not secured. Chloranil oxidation gave the \(\alpha,\beta\-
unsaturated ketone \(\text{L2}\).

(b) l-Methyl-6-phenyl-7,12-dihydropleiadene-7-one \(\text{L2}\) — The
second pale, light green-blue band from the above column consisted
of colorless crystals (0.288 g., 44.5\%) obtained on elution (crystal-
lization from benzene-Skelly Solve F), m.p. 190\(^\circ\)-220\(^\circ\); \(\nu\text{co} = 1650\text{cm}^{-1}\);
\(\lambda_{\text{max}}, 340 \mu\).

The n.m.r. spectrum (Fig. III-11) shows an increase in the number
of aromatic protons to 14 with other peaks remaining the same with
respect to ketone \(\text{L2}\).
Anal. Calcd. for C_{25}H_{16}O: C, 89.79; H, 5.43

Found: C, 90.02; H, 5.46

(c) 1-Methyl-7-phenyl-7,12-dihydropleiadene-7-ol (13) -- The third fraction from a colorless band that followed the pale, light green-blue band gave colorless crystals (0.07 g., 9.9%) (crystallization from benzene and Skelly Solve F); m.p. 175°-177°, ν OH, 3550 cm⁻¹.

Anal. Calcd. for C_{25}H_{20}O: C, 89.25; H, 5.99

Found: C, 89.20; H, 5.96

1-Methyl-6-phenyl-7,12-dihydropleiadene-7,12-dione (13) -- To a solution of 1-methyl-6-phenyl-7,12-dihydropleiadene-7-one (12) (0.200 g.) in glacial acetic acid (25 ml.) was added sodium dichromate (0.320 g.). After allowing it to reflux for 3 hours, the mixture was poured into cold water (200 ml.). The white floculant solid that formed was collected by filtration, washed with water, dissolved in methylene chloride, and dried over anhydrous magnesium sulfate. Chromatography on alumina with methylene chloride as solvent yielded white crystals (0.156 g., 74.8%), m.p. 205°.

Anal. Calcd. for C_{25}H_{16}O_2: C, 86.18; H, 4.63

Found: C, 86.05; H, 4.56

7,12-Diphenyldihydropleiadene-7,12-diol (45) -- To a solution of 7,12-dihydropleiadene-7,12-dione (44) (1.000 g.) in dry ether (100 ml.) was added phenylmagnesium bromide (3M, 5.0 ml.), and the resulting mixture was stirred at room temperature for 12 hours. The reaction mixture was then hydrolyzed with 10% hydrochloric acid. The organic layer was washed with water, dried over anhydrous magnesium sulfate
and decolorized with charcoal. After evaporation of the solvent, a small amount of absolute ethanol was added to the dark yellow oily residue to obtain small white crystals (0.622 g., 39.7%), m.p. 225°-230°.

Anal. Calcd. for C<sub>30</sub>H<sub>22</sub>O<sub>2</sub>: C, 86.93; H, 5.35
Found: C, 87.05; H, 5.18

Reaction of 1-methyl-7,12-dihydropleiadene-7-one (12) with methylmagnesium bromide — To a solution of 1-methyl-7,12-dihydropleiadene-7-one (12) (0.867 g.) in dry tetrahydrofuran (50 ml.) was added methylmagnesium bromide (3M., 10 ml.). The mixture was allowed to reflux (58°) for 24 hours, cool to room temperature, and was hydrolyzed with aqueous ammonium chloride.

The organic layer, after partitioning, was dried over anhydrous magnesium sulfate and the solvent evaporated. The resulting concentrated benzene solution was placed on an alumina column and developed with benzene. A purple-blue band, followed by a sky-blue band was observed.

(a) 1-methyl-7-exo-methylene-7,12-dihydropleiadene (48) — The fraction from the purple-blue band gave white crystals (0.16 g., 18.6%), (crystallization from benzene ethanal), m.p. 100°-101°; the IR spectrum possessed a strong band at 11.15 (Fig. I-19) characteristic of an α,β-disubstituted olefin; the UV spectrum, A<sub>max</sub> 305 m<sub>μ</sub> (Fig. II-3), which was 10 m<sub>μ</sub> longer than that for comparable saturated hydrocarbon; the n.m.r. spectrum (Fig. III-8) shows peaks for two olefinic protons.

Anal. Calcd. for C<sub>20</sub>H<sub>10</sub>: C, 93.71; H, 6.29
Found: C, 93.77; H, 6.37
(b) 1,6-Dimethyl-7,12-dihydropleiadeine-7-one (49) -- The sky blue band was cut arbitrarily in two fractions. The first fraction yielded colorless needles (about 5 mg., 1%) (crystallization from benzene-Skelly Solve F), m.p. 199°-200°.

The second fraction of the sky blue band consisted of starting material, 1-methyl monoketone 12. Unidentifiable floculant material was obtained from the last eluent solution following the two fluorescent bands.

1,6-Dimethyl-7,12-dihydropleiadeine-7-one (49): (a) Phthaloylation of 2,7-dimethylnaphthalene -- Phthalic anhydride (9.5 g., 0.064 mole) was suspended in a solution of 2,7-dimethylnaphthalene (10.0 g., 0.064 mole) in benzene (500 ml.). Aluminum chloride (21.4 g., 0.16 mole) was added during a period of 10 minutes while stirring. The reaction mixture was stirred under anhydrous conditions for 4 hours at room temperature, and was poured into 1 l. of ice-water mixed with concentrated hydrochloric acid (100 ml.). The white solid which resulted was collected by filtration, washed with water and dried to ketoacid (9 g.). The ketoacid remaining in the organic layer was extracted with aqueous sodium bicarbonate, followed by acidification. The resulting sticky solid was dried to give an additional 7 g. of material. The total yield of product was 16 g. (82.2%). The I.R. spectrum showed a broad hydroxyl band at 3.3-3.5μ and two carbonyl bands at 5.9μ and 6.0μ for acid carbonyl and keto carbonyl absorption respectively. This mixture of keto acids was used for the next step without further purification.
(b) Reduction of keto acids - - To an aqueous solution of sodium hydroxide (23 g. in 500 ml.) was added the keto acid (15 g.) obtained from (2) and zinc dust (45 g.). The reaction mixture was heated gently on a steam bath for 50 hours. After removal of the solids by filtration, the yellow-brown solution was poured into dilute hydrochloric acid. The snow white solid which formed was collected by filtration, washed with water, and digested on the steam bath with 1 l. of water for 1 hour. After filtration, the resulting solid was dried in vacuum, to give acid (13 g., 91.0%). The I.R. spectrum indicated the absence of the keto carbonyl function. Again, without purification, the acid was used for the following reaction.

(c) Cyclization of acid - - To the acid (12 g.) from (b) contained in a polyethylene bottle was introduced anhydrous liquid hydrogen fluoride (ca. 450 ml.). The dark purple solution was left standing for 48 hours while the hydrogen fluoride evaporated. The residue was treated with 10% aqueous sodium carbonate to neutralize any remaining acid and the mixture of solid and alkaline solution was treated with benzene to extract the cyclized ketone. The dark red-brown extract was washed with water, dried over anhydrous magnesium sulfate and decolorized with charcoal and the benzene solution was concentrated.

(d) Chromatography - - The concentrated benzene solution from (c) was placed on an alumina column (A) and developed with benzene. The column did not give any clear-cut bands. The first blue band was partly overlapped with the dark yellow band that followed and gave on evaporation of the eluent solvent, a very small amount of floculant
solid residue which was discarded. The solution from the dark yellow band was concentrated, and slightly greenish-white needles (5.54 g.) were obtained. Further crystallization did not take place readily. The mother liquor (1.03 g.) was rechromatographed (column B) to give the same compound (1.03 g.) as above from the first eluent solution. The second fraction gave an isomeric ketone (0.29 g.) (indicated by the I.R. spectrum). The faint yellow band that followed the second dark yellow band (not clear-cut separation) in the first column (A) was rechromatographed to obtain two new isomeric ketones (total of about 0.3 g.) characterized by their I.R. spectra. No attempt was made to determine the structures of these minor isomers. The major isomer (6.57 g., 58.3%, based on acid; 37.5%, based on 2,7-dimethyl-naphthalene), m.p. 174°; lit. 174° is identical in every aspect with the compound resulting from 1,4-addition of methyl Grignard bromide to 1-methyl-7,12-dihydropleiadene-7-one (12) (see Section B), and therefore, this major isomer is assigned 1,6-dimethyl-7,12-dihydropleiadene-7-one (49).

1,6-Dimethyl-7,12-dihydropleiadene (5) - - To a suspension of lithium aluminum hydride (2 g., excess) in dry ether (250 ml.) was added aluminum chloride (2.5 g.) dissolved in ether (30 ml.). The mixture was refluxed for 48 hours in a Soxhlet apparatus containing 2,6-dimethyl-7,12-dihydropleiadene-7-one (49) (2.50 g.). After the slow introduction of water (100 ml.) into the reaction flask to hydrolyze the reaction mixture, the two phase system was poured into concentrated hydrochloric acid (100 ml.). The organic layer was diluted with benzene (100 ml.), separated, washed with water and
dried over anhydrous magnesium sulfate. The residue resulting from evaporation of the solvent was chromatographed on alumina, using benzene as an eluant. Crystallization from benzene-absolute ethanol yielded white fabric needles (1.79 g., 75.5%), m.p. 130°-131°; lit.⁹ 133°.

**1,6-Dimethyl-7,12-dihydropleiadene-7,12-sulfide (6): Method A —**

A mixture of 1,6-dimethyl-7,12-dihydropleiadene (1.000 g., 0.00388 mole) and powdered sulfur (0.249 g., 0.00776 mole) in a small distilling flask with a condenser was placed in a salt bath at 180°, and the temperature was raised rapidly. Evolution of hydrogen sulfide began about at 200°, and then became fast at around 260°. Heating was continued at 260° ± 5° for 7 to 8 minutes until the evolution of the gas was no longer observed. The reaction mixture was dissolved in benzene and the dark-red solution was decolorized with charcoal. The concentrated solution was placed on an alumina column, and developed with benzene. Crystallization from benzene-Skelly Solve F gave orange needles (0.309 g., 28.1%), m.p. 220°, lit.⁵ 217°.

**Method B —** A mixture of 1,6-dimethyl-7,12-dihydropleiadene-7,12-diol (64) (0.50 g.), phosphorus pentasulfide (1 g.) and carbon disulfide (100 ml.) was stirred for two days at room temperature. The resulting reaction mixture was filtered with suction through a celite mat. The solvent was evaporated and the residue was chromatographed on grade I alumina using benzene as an eluent. Crystallization from benzene-Skelly Solve F gave colorless prisms (0.34 g., 70.5%), m.p. 222°-223°. I.R. and n.m.r. spectra showed this compound to be identical with that obtained in the Method A.
Anal. Calcd. for C_{20}H_{16}S: C, 83.31; H, 5.59; S, 11.10
Found: C, 83.13; H, 5.76; S, 11.25

1,6-Dimethyl-7,12-dihydropleiadene-7,12-dione (63) - - To a solution of 1,6-dimethyl-7,12-dihydropleiadene-7-one (69) (1.200 g.) in glacial acetic acid (100 ml.) was added sodium dichromate (2.0 g.). The mixture was refluxed for 3 hours and then poured into ice water. White crystals formed were collected by filtration, dried and chromatographed on alumina using chloroform as an eluent solvent. Crystallization from chloroform-Skelly Solve F gave white prisms (0.962 g., 76.2%), m.p. 215°-216°, lit. 4, 216°.

1,6-Dimethyl-7,12-dihydropleiadene-7,12-diol (64) - - To a solution of 1,6-dimethyl-7,12-dihydropleiadene-7,12-dione (63) (0.880 g.) in benzene (100 ml.) was added absolute ethanol (200 ml.), followed by sodium borohydride (2 g.). The mixture was heated gently until dissolution of the reagent was complete. It was then allowed to stand overnight at room temperature. To the reaction mixture was added water (100 ml.) and the resulting solution was heated on a steam bath for 30 minutes. The organic layer containing suspension of white crystals was separated from aqueous layer, followed by addition of benzene to dissolve the crystals completely. The organic solution was dried over anhydrous magnesium sulfate and the solvent was evaporated. The solid residue was crystallized from acetone-Skelly-Solve F to give white crystals, (0.715 g., 80.0%), m.p. 189°-190°.

1,6-Dimethyl-7,12-dihydropleiadene-7,12-sulfone (15) - - To a solution of 1,6-dimethyl-7,12-dihydropleiadene-7,12-sulfide (6)
(0.400 g.) in benzene (5 ml.) was added glacial acetic acid (10 ml.), and peracetic acid (8 ml.). The mixture was stirred overnight at room temperature. Water (50 ml.) was added to the resulting reaction mixture and the product was extracted with chloroform. The organic solution was dried over anhydrous magnesium sulfate and the solvent was evaporated; the residue was chromatographed on alumina using 1:1 mixture of benzene and chloroform as an eluent. Crystallization from chloroform-Skelly Solve F gave colorless plates (0.36 g., 79.8%), m.p. 220°-230° (dec.).

Anal. Calcd. for C_{20}H_{16}SO_2: C, 74.99; H, 5.03; S, 9.99
Found: C, 74.85; H, 5.07; S, 10.06

Diels-Alder Adduct 65 of 1,6-Dimethyl-7,12-dihydropleiadene-7,12-sulfone (15) and N-Phenylmaleimide — A mixture of the sulfone (0.100 g.) and N-phenylmaleimide (0.200 g., excess) was heated in an open test tube in a salt bath at 220°-240° (ca. 8 min.), until evolution of sulfur dioxide was complete. The resulting brown solid was washed with cyclohexane to remove excess N-phenylmaleimide, and the residual solid was chromatographed on alumina using benzene as the eluent solvent. Crystallization from benzene-Skelly Solve F yielded colorless prisms (0.070 g., 51.3%), m.p. 310°-311°.

Anal. Calcd. for C_{30}H_{23}NO_2: C, 83.89; H, 5.40; N, 3.26
Found: C, 83.69; H, 5.41, N, 3.10

Dimer 66 of 1,6-Dimethylpleiadene (14): A Photolysis of Sulfone 15 — A solution of 1,6-dimethyl-7,12-dihydropleiadene-7,12-sulfone (15) (0.120 g.) in benzene (180 ml.) was irradiated with a mercury arc at 20° under a nitrogen atmosphere (1 atm.) for one hour. The
resulting solution was concentrated and chromatographed on grade I alumina using benzene as an eluent solvent. A bright blue fluorescent band moving rapidly was observed. The solid residue formed on evaporation of the eluate of this fraction was crystallized from benzene-ethanol yielding faint yellow needles (0.024 g., 12.5%), m.p. > 405°.

Anal. Calcd. for C_{40}H_{32}: C, 93.71; H, 6.29
Found: C, 93.73; H, 6.54

B. Pyrolysis of Sulfone 15

--- 1,6-Dimethyl-7,12-dihydro-pleiadene-7,12-sulfone (15) (0.100 g.) was heated in an open test tube at 220°-240° until the evolution of sulfur dioxide was complete (about 8 min.). The brown solid which formed was dissolved in benzene and decolorized with charcoal. The concentrated solution was chromatographed and crystallized as described in A. to give yellow needles (0.022 g., 13.8%), m.p. > 405°. This product was found to be identical (I.R. spectrum) with the compound obtained from the photolysis of sulfone 15.
PART II. INDENO(1,2,3-cd)PLEIADENE

INTRODUCTION

The synthesis of indeno(1,2,3-cd)pleiadene (67) was undertaken as part of a study of structural modification on the stability of the pleiadene system. Although the pleiades (1, 8, 23 7, 4, 68, 8, 23 and 698, 23) synthesized thus far have been shown to be highly reactive and incapable of isolation, acepleiadylene (69) was found by Schlessinger8, 23 to have limited stability in that it exists as a blue colored species in solution for a short period of time. Since this greater stabilization may be due to an increase in conjugation within the

\[ \text{Diagram of molecules} \]

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molecule compared to simple pleiadene, a further increase in conjugation might be expected to stabilize the pleiadene skeleton to an even greater extent. It might be possible, therefore, to synthesize a stable and isolable pleiadene species by suitable annulation. In this respect, it seemed of interest to attempt the synthesis of indene(1,2,3-cd)pleiadene (67).
DISCUSSION OF RESULTS

The only two previously reported compounds in the indeno-(1,2,3-cd)pleiadene (67) series are indeno(1,2,3-cd)-9,14-dihydropleiadene-9,14-dione (74), and indeno(1,2,3-cd)-9,14-dihydropleiadene (73), which were originally named as 4,5-phthaloylfluoranthenes and 4,5-oxydenefluoranthenes, respectively. Campbell and his co-workers observed that a colorless hydrocarbon, m.p. 208°-210° was formed in low yield in addition to anthracene derivative 72 and anthraquinone derivative 71, when 4-o-tolucylfluoranthenes 70 was subjected to the Elbs reaction.25


The anthraquinone derivative 71 was readily identified by comparison with an authentic sample from an independent synthesis.26 The anthracene derivative 72 was identified by oxidation to the corresponding anthraquinone 71. The hydrocarbon 73 could be distinguished from the anthracene derivative 72 by the fact that chromic acid oxidation of this compound gave a diketone 74 which was not identical with the anthraquinone derivative 71. The formation of the same diketone 74 (yield not mentioned) and of the anthraquinone derivative 71 (yield, 20 mg. out of 1.1 g. of ketoacid 75) was also observed by these workers27 in the aluminum chloride-sodium chloride fusion reaction of 4-benzoylfluoranthen - 2'-carboxylic acid (75). This new diketone 74, a yellow crystalline compound, m.p. 296°-297° was distinguished from 71 by the fact that the former gave a red color with concentrated sulfuric acid and no vat color with sodium dithionate, whereas the

anthraquinone derivative 71 showed a bluish-green color with concentrated sulfuric acid and a bluish-violet vat color with alkaline dithionate. In particular, the negative vat test indicated that the diketone 74 was not an anthraquinone derivative isomorphic with 71.

In the present study, an improved synthesis of the diketone 74, the starting material leading to the desired indeno(1,2,3-cd)pleiadene (67), was initiated with a study of the Fiedel-Crafts condensation of fluoranthene and phthalic anhydride. This Fiedel-Crafts reaction was complicated by the formation of a mixture of difficultly separable isomeric ketoacids. The earlier reported27, 28 phthaloylation of fluoranthene was carried out in refluxing carbon disulfide for 60 hours in the presence of aluminum chloride. Campbell and


co-workers\textsuperscript{28} reported that when fluoranthene (20 g.) was treated with phthalic anhydride as described by von Braun and Manz,\textsuperscript{27} there was obtained a crude product (14 g.) (a mixture of two ketoacids 75 and 76) which was too strongly adsorbed on alumina to be purified by alumina chromatography. They found that separation of the isomeric ketoacids could be effected indirectly by conversion of the acid mixture into the corresponding methyl esters (using methanol and sulfuric acid), followed by chromatographic separation of the esters 77 and 78 and subsequent alkaline hydrolysis of the individual esters.
The presently modified phthaloylation reaction was carried out in benzene at room temperature with stirring for 3 hours and produced in 95% yield a clean yellow solid mixture of 4'-benzoylfluoranthene - 2'-carboxylic acid 75 and 11-benzoylfluoranthene - 2'-carboxylic acid 76. Esterification of the mixture of keto acids with methanol and acetyl chloride,\(^{29}\) which proceeded rapidly, gave a mixture of esters 77 and 78 in much higher yield (82%) than that obtained by Campbell and co-workers.

\[
\begin{align*}
\text{(75)} & \quad \text{+} \quad \text{(76)} & \quad \text{CH}_3\text{COCl} & \quad \text{CH}_3\text{OH} & \quad \text{(77)} & \quad \text{(78)}
\end{align*}
\]

The mixture of esters separated by alumina chromatography according to Campbell and co-workers,\(^{28}\) but the separation was difficult and the procedure reported by the above authors was not practical for preparative scale work. A good separation procedure was finally developed, as described in the experimental section of this thesis.

Since cyclization of the acid 75 as carried out by Campbell and co-workers\(^{24}\) gave poor results, and in view of Fieser's report\(^9\) that

\(^{29}\) Private communication with Dr. R. Stein, who has unpublished results on this type of esterification during his work under Professor M. P. Cava.
the methyl esters of some similar keto acids cyclize more readily than the free acids, cyclization of the ester 77 was carried out. The desired diketone 74 was obtained in 39% yield under conditions similar to those used by Campbell and co-workers for the cyclization of the acid 75.

\[
\begin{align*}
77 & \xrightarrow{\text{AlCl}_3, \text{NaCl}, \Delta} 74 \\
75 & \xrightarrow{\text{AlCl}_3, \text{NaCl}, \Delta} 74 + 71
\end{align*}
\]

Campbell and co-workers reported that the cyclization of the keto acid 75 gave, in addition to diketone 74, a small amount of the anthraquinone derivative 71. No such by-product was found in the present study of the cyclization of the methyl ester 77. The diketone structure 74 was confirmed by a negative sodium dithionate test.

The LiAlH₄-AlCl₃ reduction of diketone 74 gave the expected hydrocarbon 73. As mentioned earlier, the formation of this hydrocarbon in low yield had been noted by Campbell and co-workers as one of three products in the Elbs reaction of 4-o-tolуlfluoranthen (70). The diketone 74 was converted into diol 79 with sodium
Using phosphorus pentasulfide, the diol was converted to the crystalline sulfide 80, which in turn was transformed to sulfone 81, a pale yellow crystalline compound, by peracetic acid oxidation.

Although this sulfone was found to decompose at 210°-230° in the absence of a solvent, it was much less stable in solution, decomposing already at about 80°. When a solution of sulfone 81 in benzene was heated on the steam bath, the solution gave a transient blue-violet color which soon turned to a permanent pale yellow. From this yellow solution a greenish-yellow crystalline dimer 82 was separated in 27.5% yield. The blue-violet color was attributed to indeno(1,2,3-cd)-
pleiadene (67), and the turning of this color to yellow was accountable for in its dimerization. Schlessinger\(^2\) reported that ace-pleiadylene (69) may be observed as transient blue color in solution before it dimerizes.

In qualitative terms based upon an observable colored species in solution, acepleiadylene (69) and indeno(1,2,3-acd)pleiadene (67) seem to have roughly the same order of stability. Acepleiadylene (69) was generated by acid catalized dehydration of diol 83, since the precursor sulfone 84 was not stable enough to isolate. The formation of this sulfone was inferred only indirectly by the fact that when a blue solution of acepleiadylene (69) was treated with
sulfur dioxide,\textsuperscript{30} the blue color disappeared faster than that of a blank solution, and then returned briefly on mild warming.

These observations indicate that the sulfone precursor 8\textsubscript{1} of indeno(1,2,3-cd)pleiadene (67) is somewhat more stable than the sulfone precursor 8\textsubscript{4} of acepleiadylene (69). Since the thermal stability of a precursor sulfone should be inversely proportional to the stability of the corresponding pleiadene, it appears that indeno-(1,2,3-cd)pleiadene (67) is actually less stable species than acepleiadylene (69), contrary to the original expectation.

The indenopleiadene 67 could be trapped when generated thermally at 80\degree. When a solution of the sulfone 8\textsubscript{1} and N-phenylmaleimide

\textsuperscript{30}The reaction was based on the observation by Jensen and Coleman \textit{J. Am. Chem. Soc.}, 80, 6149 (1958) that 1,2-diphenylbezocyclobutene (i) in refluxing carbon tetrachloride reacts with sulfur dioxide to give 1,3-dihydro-1,3-diphenylisothianaphthene-2,2-dioxide (iii) presumably through the intermediate \(\alpha,\alpha'-\text{diphenyl-o-quinomethane} (ii)\).
in benzene was heated on a steam bath, crystalline adduct m.p. 315°, was formed in 46% yield. From the same consideration as used in the assignment of structure of the N-phenylmaleimide adduct of 1-methylpleiadene (7) and of 1,6-dimethylpleiadene (4) (Part I of this thesis), this adduct was assigned the \textit{exo} configuration 85 rather than the \textit{endo} configuration 86.

As was the case with 1-methylpleiadene dimer, 35 and 36 and 1,6-dimethylpleiadene dimer (66), indeno(1,2,3-cd)pleiadene dimer could possess either \textit{syn} configuration 87 or \textit{anti} configuration 88. By
analogy to the previously considered systems, the anti configuration has been assigned to this dimer.

Photolytic extrusion of sulfur dioxide from the sulfone was next attempted. Surprisingly, the irradiation of sulfone in benzene at room temperature for one hour in air or under a nitrogen atmosphere did not give the anticipated dimer, but produced a mixture of two new compounds. When the concentrated photolyzed solution was chromatographed in benzene on alumina, two light green fluorescent bands separated by colorless zone were observed. The fraction from the lower band gave a small amount of light greenish-yellow crystalline compound, m.p. 222°-227°, designated as unknown A; from upper band, a pale greenish-yellow crystalline compound, m.p. 230°-232°, designated as unknown B, was obtained in a larger amount. Since the sulfone photolyses both in air and under nitrogen gave the same result, it was first thought that these two compounds might have been formed by the solvent participation. Thus, as a simple control experiment, the photolysis was carried out in nitrobenzene solution, in the hope that the nitrobenzene might give compounds different from those formed in benzene. After removal of the nitrobenzene from the reaction mixture by steam distillation, only one product, identical with the unknown B, was obtained in lower yield than that obtained from the reaction in benzene, suggesting that at least the unknown B was not formed by solvent participation. The fate of unknown A, however, was uncertain in this reaction. It was then suspected that the oxygen contained in the solvent was involved in the reaction;
therefore, another experiment was carried out in a large amount of carbon disulfide in the open air at room temperature. From this reaction both unknowns A and B were obtained. Again, compound B was the major product and was found in better yield than in the benzene reaction.

From the above results, it appeared that unknowns A and B might be peroxides formed by reaction of indenopleiadene with oxygen in the solvent. Carbon and hydrogen analysis of unknown B gave C, 85.98; H, 4.08 which are in good agreement with the calculated values (C, 86.18; H, 4.22) for C_{24}H_{14}O_{2} as a peroxide 89. The observed molecular weight (339 and 361) for unknown B as determined osmometrically also agree reasonably with the calculated value (334) for the peroxide structure 89. The ultraviolet spectrum of unknown B (Fig. II - 12) is quite similar to that of the corresponding diol 79; its n. m. r. spectrum (Fig. III - 7) shows a singlet peak at 3.60 τ (2 protons) comparable to that at 3.95 τ (2 protons) for the benzylic protons in the known oxide 90.31

31 The sample of this oxide was furnished by Dr. R. H. Schlessinger.
The n.m.r. spectrum of unknown A was not obtained due to the poor solubility of the sample in the usual organic solvents. The ultraviolet spectrum of A is identical with that of unknown B. Osmometric molecular weight determination of A gave values of 405 and 540. Since the solutions of the sample used were very dilute, there was considerable uncertainty in these observed values. Nevertheless, the molecular weight data seemed to indicate that this compound might not be monomeric. This view was partially supported by the fact that unknown A was much less soluble in various solvents compared with compound B. Thus, it is proposed that compound A may be a dimeric peroxide; such a compound may have either the *syn* configuration 91 or the *anti* configuration 92. The elemental analysis for unknown A gave

values of C, 85.70 and H, 4.29 which are in accord with those (C, 86.18; H, 4.22) calculated for the dimeric peroxide 91 or 92.
The oxide structure 93, while in accord with the observed spectral data of A or B, was excluded from serious consideration because of the determined analytical results.

It is noteworthy that oxides were formed instead of indenopleiadene dimer 88 in the photolysis of the precursor sulfone 81, whereas indenopleiadene dimer 88 was obtained as expected in the thermolysis of the sulfone in the solution. It is also significant that in the previously investigated simpler pleiadene series, only pleiadene dimers, and not oxides, were obtained in the photolysis of the precursor sulfones 11, 15, 29, etc., under comparable conditions.

Most likely, the species generated by the extrusion of sulfur dioxide in the photolysis of sulfones 11, 15, 29, etc., are singlets which give rise to the observed dimers. The intermediate generated by the thermolysis of indenopleiadene sulfone 81 appears to be a similar type of species, since it also affords a dimeric hydrocarbon. On the other hand, the intermediate formed during the photolysis of sulfone 81 appears to be in the triplet state, since it readily traps oxygen from the solution.

It is possible that the triplet form of indenopleiadene may have been formed either directly from the sulfone (81) on the photolytic
extrusion of sulfur dioxide or via photo-excitation of the singlet state of the hydrocarbon generated initially from the sulfone. The choice between these two alternatives, however, cannot be made on the basis of the small amount of evidence available from the present study.
Phthaloylation of Fluoranthene -- To a suspension of finely ground phthalic anhydride (36.6 g.) in a solution of fluoranthene (50 g.) in benzene (1 l.) was added aluminum chloride (82.5 g.) during a period of 10 minutes while stirring. After stirring for 3 hours at room temperature, the reaction mixture was poured into ice-water (2 l.) mixed with concentrated hydrochloric acid (200 ml.). The bright yellow crystals were suspended in aqueous layer collected by filtration, washed with water and dried to give (73.7 g.) of mixture of 4-benzoylfluoranthene-2'-carboxylic acid (75) and 11-benzoylfluoranthene-2'-carboxylic acid (76). The mixture of ketoacids remaining in the benzene layer was extracted with aqueous sodium bicarbonate. On acidification, an additional 8.7 g. were obtained, yielding a total of 82.4 g. (95%).

Methyl 4-benzoylfluoranthene-2'-carboxylate (77): A. Esterification -- To a solution of the mixture (70 g.) of 4-benzoylfluoranthene-2'-carboxylic acid (75) and 11-benzoylfluoranthene-2'-carboxylic acid (76) in absolute methanol (1200 ml.) was added acetyl chloride (300 ml.) dropwise while stirring at room temperature. The mixture was refluxed for one hour. After standing for 2 hours 17.5 g. of yellow crystals of methyl 8-benzoylfluoranthene-2'-carboxylate was collected by filtration. Subsequent crystallization were effected
by addition of a little water to the mother liquor to obtain 41.6 g. of yellow material as a mixture of methyl 4-benzoylfluoranthene-2'-carboxylate and methyl 11-benzoylfluoranthene-2'-carboxylate, giving the total of 59.1 g. (81.4%). These two esters were separated by the following procedure.28

B. Chromatography - A solution of the mixture (10 g.) of the above two esters in benzene was concentrated, placed on a 1/4" X 40" alumina column and developed with 3:1 benzene-Skelly Solve B. Two blue fluorescent bands were separated by a yellow band. The first blue band gave oily residue on evaporation of the eluent solvent, which was discarded. The yellow band gave 5.5 g. of methyl 3-benzoylfluoranthene-2'-carboxylate, yellow crystals, m.p. 110°-112°; lit.28 103°-105°, after crystallization from ethanol and a small amount of water. The upper blue band yielded 2.5 g. of methyl-benzoylfluoranthene-2'-carboxylate, yellow crystals, m.p. 170°-172°; lit.28 172°-174°, when crystallized from ethanol and a small amount of water.

Indeno(1,2,3-cd)-9,14-dihydropleiadene-9,14-dione (74) - - A mixture of aluminum chloride (20 g.) and sodium chloride (5 g.) in a beaker was fused at 140° and cooled to 110°. To this fusion was added methyl 4-benzoylfluoranthene-2'-carboxylate (77) (5.0 g.) during the period of 3 to 5 minutes, while stirring and scrambling down the side of the beaker. The black reaction mixture was cooled
to 80°, heated to 160°, cooled to 100°, heated to 160°, cooled to 140°, and poured into ice-water. The mixture and the container were placed on a steam bath for an hour. The brown solid was collected by filtration, dried, and refluxed with benzene for one hour to remove insoluble material (2.2 g.). The benzene solution was dried and washed with a mixture of anhydrous magnesium sulfate and activated charcoal. The dark brown solid residue resulting from evaporation of the solvent was chromatographed on alumina, using benzene as a developer. The eluent solution from dark yellow band was concentrated, and crystallization was effected by addition of Skelly Solve F to give orange yellow needles, diketone (1.8 g., 38.5%), m.p. 295°; lit. 296°.

Anal. Calcd. for C_{24}H_{20}: C, 86.73; H, 3.64

Found: C, 86.96; H, 3.76

Indeno(1,2,3-cd)-9,14-dihydropleiadene (73) — To a suspension of lithium aluminum hydride (0.2 g.) in dry ether (125 ml.) was added aluminum chloride (2 g.) dissolved in dry ether (30 ml.). The mixture was refluxed for 2 days in a Soxhlet apparatus containing indeno-(1,2,3-cd)-9,14-dihydropleiadene-9,14-dione (74). After introducing water (50 ml.) slowly into the reaction flask to hydrolize the reaction mixture, the two-phase system was poured into concentrated hydrochloric acid (50 ml.). The organic layer was diluted with benzene (100 ml.), partitioned, washed with water, and dried over anhydrous magnesium sulfate. The yellow oily residue obtained on evaporation of the solvent was chromatographed on alumina, using benzene as a developer. Crystallization from benzene-ethanol yielded light yellow
needles (0.14 g., 74.5%), m.p. 210°-213°; lit.\textsuperscript{24} 208°-210°. Recrystallization gave fine greenish yellow needles, m.p. 218°-219°. This hydrocarbon gives a pink color when heated with concentrated sulfuric acid as reported.\textsuperscript{24}

Anal. Calcd. for C\textsubscript{24}H\textsubscript{16}: C, 94.70; H, 5.30

Found: C, 94.53; H, 5.21

\textbf{Indeno(1,2,3-cd)-9,14-dihydropleiadene-9,14-diol (79)} -- To a hot solution of indeno(1,2,3-cd)-9,14-dihydropleiadene-9,14-dione (74) (1.155 g.) in benzene (200 ml.) was added absolute ethanol (200 ml.), followed by sodium borohydride (2.5 g.). The mixture was boiled for 10 minutes, and allowed to stand for 6 hours. The resulting reaction mixture was hydrolyzed with water and placed on a steam bath for 0.5 hours. After partitioning, the organic layer was washed with water, and dried over anhydrous magnesium sulfate. Crystallization from benzene yielded pale yellow needles, (0.952 g.) m.p. 205°-206°. The crude product obtained from the aqueous portion by treatment with a large amount of water, was dried and crystallized from benzene to give the diol (0.052 g.). The total yield of the product was 1.004 g. (86.5%).

Anal. Calcd. for C\textsubscript{24}H\textsubscript{16}O\textsubscript{2}: C, 85.69; H, 4.79

Found: C, 85.48; H, 4.78

\textbf{Indeno(1,2,3-cd)-9,14-dihydropleiadene-9,14-sulfide (80)} -- To a solution of indeno(1,2,3-cd)-9,14-dihydropleiadene-9,14-diol (79) (0.424 g.) in carbon disulfide (125 ml.) was added phosphorus pentasulfide (0.5 g.). The mixture was stirred at room temperature
for 33 hours. After removing solid material by filtration, the solvent was evaporated and the residue was dissolved in benzene. The benzene solution was concentrated and chromatographed on alumina, using benzene as a developer. The column gave a dull green fluorescent band. Crystallization from benzene and Skelly Solve F yielded shiny greenish yellow plates (0.338 g., 88.2%), m.p. 270°-276°.

Anal. Calcd. for C$_{24}$H$_{14}$O$_2$: C, 86.21; H, 4.22
Found: C, 86.10; H, 4.23

Indeno(1,2,3-cd)-9,ll-dihydropleiadene-9,ll-sulfone (81) - - A solution of indeno(1,2,3-cd)-9,ll-dihydropleiadene-9,ll-sulfide (80) (0.457 g.) in benzene (10 ml.) was cooled to room temperature. To this solution was added glacial acetic acid (6 ml.), followed by peracetic acid (3 ml.). The mixture was stirred for 9 hours at room temperature. The pale yellow crystals formed were collected by filtration and dried to give 0.410 g. of product. The mother liquor was treated with water, and after removing the aqueous layer, Skelly Solve F was added to the benzene solution to obtain sulfone (0.035 g.). The total yield was 0.445 g. (88.7%). The colorless benzene solution of sulfone turns blue when boiled.

Anal. Calcd. for C$_{24}$H$_{14}$SO$_2$: C, 78.68; H, 3.85; S, 8.75
Found: C, 78.97; H, 4.04; S, 8.64

Diels-Alder Adduct 85 of Indeno(1,2,3-cd)-9,ll-dihydropleiadene-9,ll-sulfone (81) and N-Phenylmaleimide - - A mixture of the sulfone (0.050 g.) and N-phenylmaleimide (0.500 g.) in a 10 ml. flask was placed on a steam bath. Soon evolution of sulfur dioxide was observed, while the mixture was melting. After heating for 30 minutes,
the reaction mixture was treated with hot cyclohexane to remove excess N-phenylmaleimide. The cyclohexane-insoluble material, weighing 0.50 g., was dissolved in benzene, placed on an alumina column and developed with benzene. Two blue bands separated by a colorless zone were observed. The first band gave a very small amount of floculant material on evaporation of solvent from the eluate, which was not investigated further. The solution from the second (upper) band was concentrated, and mixed with a little Skelly Solve F to obtain colorless plates (0.030 g., 46%), m.p., 315°.

Anal. Calcd. for C₃₄H₂₁NO₂:  C, 85.87; H, 4.45; N, 2.95
Found:  C, 85.97; H, 4.51, N, 3.03

Dimer 88 of Indeno(1,2,3-cd)pleiadene (67) - - A solution of indeno(1,2,3-cd)-9,14-dihydropleiadene-9,14-sulfone (81) (0.050 g.) in 50 ml. of benzene (incompletely dissolved at room temperature) was heated on the steam bath under reflux. Soon the colorless solution turned blue and the blue color lasted for about 15 minutes and was replaced by a permanent yellow color. The refluxing was continued for 30 minutes. The solution was then allowed to stand at room temperature giving a pale greenish yellow microcrystalline solid, m.p. 405°. A further crop was obtained by adding a little ethanol to the mother liquor; the total product was 0.022 g. (27.5%).

Anal. Calcd. for C₄₈H₂₈:  C, 95.30; H, 4.70
Found:  C, 95.26; H, 4.74

Photolysis of Indeno(1,2,3-cd)-9,14-dihydropleiadene-9,14-sulfone (81) - - (a) A solution of the sulfone (50 mg.) in benzene (170 ml.) was irradiated with a mercury arc at 20° under nitrogen
atmosphere for one hour. After evaporating the solvent from the resulting reaction mixture, the solid residue was dissolved in a small amount of methylene chloride, placed on an 5/8" X 7" alumina column, and eluted with benzene. Two yellow-green fluorescent bands separated by a colorless zone were observed. The solid residue formed on evaporation of the solvent from the eluate of lower band was crystallized from benzene-Skelly Solve F to give light greenish yellow needles (6 mg.), m.p. 225°-227° (designated as compound A). The upper band, after workup in the same fashion, gave pale greenish yellow needles (7 mg.), m.p. 230°-232° (designated as compound B).

(b) The same reaction was carried out in the air, and the reaction mixture was worked up as described above to obtain compound A (6 mg.) and compound B (9 mg.).

(c) The same reaction was carried out in air using nitrobenzene (120 ml.) as the solvent. The resulting reaction mixture was steam distilled to remove nitrobenzene and the solid residue which remained suspended in water in the distilling flask was collected by filtration, dried, and chromatographed as described above. A blue fluorescent band and a yellow-green band following it were observed. From the blue band, a small amount of an unidentifiable amorphous material was obtained. The material from the yellow-green band was compound B (3 mg.).

(d) The same reaction was carried out in the air using carbon disulfide (400 ml.) as the solvent, yielding A (3 mg.) and B (15 mg.).
Anal. Compound A. Found: C, 85.70; H, 4.29
Calcd. for proposed Structure 91 or 92 C, 86.18; H, 4.22
Compound B. Found: C, 85.98; H, 4.08
Calcd. for proposed Structure 89 C, 86.18; H, 4.22
APPENDIX I. INFRARED SPECTRA
APPENDIX II. ULTRAVIOLET SPECTRA
Fig. II-2

Absorbance

Wavelength (m\(\mu\))

296 (\(\log \epsilon = 4.11\))

98% EtOH

max

\(\lambda\)
Fig. II-3
Fig. II-4

Absorbance

Wavelength (m\(\mu\))

\(\lambda_{max}^{95\%\text{ EtOH}}\):
- 283 (\(\log \epsilon = 4.16\))
- 294 (\(\log \epsilon = 4.46\))

95\% EtOH
Fig. II-5

Wavelength (m\(\mu\))

Absorbance

298 (log \(\varepsilon\) 4.20 approx.)

\(\lambda_{max}^{95\%}\) EtOH
Fig: II - 6

95% EtOH 308 (log $\varepsilon$ 4.40)

Wavelength (m$\mu$)
Fig. II-7
Fig. II-8
Fig. II - 9

Absorbance

Wavelength (mµ)

$\lambda_{\text{max}}$ 340 (log $\varepsilon$ 4.99)

95% EtOH
Fig. II-11

Absorbance

λ max 95% EtOH 289 (log ε 4.73)

λ max 95% EtOH 300 (log ε 4.83)

Wavelength (mμ)

200 260 300 350 390

A
Fig. II-12

Absorbance

Wavelength (mμ)

95% EtOH max, 289 (log ε 4.22)

95% EtOH max, 300 (log ε 4.46)
APPENDIX III. N.M.R. SPECTRA
Fig. III-1

Magnetic field sweep, $\delta$

P.P.M.

T.M.S.

2.36-2.92 $\tau$

5.58 $\tau$

7.42 $\tau$

$\delta$

P.P.M.
Fig. III-2
Fig. III-3
Fig. III - 5

Magnetic field sweep, \( \theta \)

- 2.33 \( \tau \)
- 3.15 \( \tau \)
- 4.74 \( \tau \)

T.M.S.
Fig. III-7
Fig. III - 8

Magnetic field sweep, δ

242, 2.90, 4.29, 4.33, 4.72, 5.67, 7.39

T.M.S.
Fig. III-9
Fig. III-12